

1                   **IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

2                                   **TITLE OF THE INVENTION**

3   Bilge Water Reclamation System and Process.

4                                   **CROSS-REFERENCE TO RELATED APPLICATIONS**

5           This application claims the benefit of the filing date of U.S. Provisional Patent  
6   application number 60/414,810 filed in the United States Patent and Trademark Office on  
7   September 30, 2002.

8                                   **STATEMENT REGARDING FEDERALLY SPONSORED**

9                                   **RESEARCH OR DEVELOPMENT**

10   Not Applicable.

11                                  **BACKGROUND OF THE INVENTION**


12           Field of the Invention. This invention relates to a process to treat a fluid column  
13   by removing organics, metals and other non-organic contaminants, and provides  
14   discharge within regulatory and environmental limits. The invention includes design of  
15   an improved electrical treatment process, a process flow allowing rapid and economical  
16   treatment of a contaminated fluid column. The invention also includes a process for  
17   regenerating activated carbon as an active unit of the treatment process.

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Date: 9/30/2003

  
Kenneth A. Keeling  
Registration No. 31,842

1           Description of the Related Art. Processes to treat water contaminated with  
2 dissolved and suspended organic materials have existed for many years. One of the  
3 largest contributors to contamination of the world's beaches is the dumping of bilge water  
4 at sea. The hydrocarbons contained in bilge water are one of the many sources of tar  
5 balls that show up on the beaches. A very small amount of hydrocarbons dissolved in  
6 seawater will adversely affect plankton population.

7           A wide variety of chemical and mechanical processes have been developed to  
8 treat contaminated fluid columns. Typically, techniques known to the prior art attempt to  
9 remove the dissolved and suspended contaminants utilizing chemical or mechanical  
10 processes to coalesce the impurities allowing removal by filtration, centrifuges,  
11 separators, or clarifiers. Prior art processes attempt to remove hydrocarbons by  
12 absorption, oxidation or ultra-filtration. Some patents that disclose such efforts are as  
13 follows:

14           U.S. Patent No. 3,969,245, issued to Ramirez on July 13, 1976, teaches an  
15 electrocoagulation system for removing pollutants from wastewater including: flowing  
16 wastewater through an electrocoagulation cell having rod-shaped electrodes to produce  
17 an embryo floc; treating the wastewater with a flocculant to form a full floc; creating  
18 laminar flow and skimming the floc.

19           U.S. Patent 5,178,755, issued to LaCrosse on January 12, 1993, teaches an  
20 ultraviolet enhanced ozone wastewater treatment system including: mixing ozone with  
21 wastewater; removing suspended solids in a multi-stage clarifier; exposing clarified  
22 effluent to ultraviolet radiation (to reduce bacteria and generate OH radicals);

1 recirculating the effluent for additional ozone injection and UV irradiation, and filtering  
2 effluent.

3 U.S. Patent 5,234,606, issued to Karazma et al. on August 10, 1993, teaches a  
4 method for treating water polluted by organic chlorine compound including: adding  
5 oxidizing agent to raw water disinfect bacteria; removing suspended solids; irradiating  
6 the raw water with ultraviolet rays to decompose organic chlorine compounds, and  
7 reducing residual oxidizing agents by activated carbon and catalytic resin.

8 U.S. Patent 5,560,831, issued to Bladen et al. on October 1, 1996, teaches a  
9 method for washing agricultural products including feeding water containing  
10 contaminants washed from agricultural products to a series of coagulation steps (feeding  
11 the underflow of the second and successive compartments); treating ultimate underflow  
12 with ozone and recirculating underflow to wash agricultural products.

13 U.S. Patent 5,679,257, issued to Coate et al. on October 21, 1997, teaches a  
14 wastewater system including adjusting PH value; applying ozone and ultrasound;  
15 applying ozone and ultraviolet light, and applying a magnetic field and an  
16 electrochemical process. The system further includes filtering steps.

17 U.S. Patent 5,888,403, issued to Hayashi on March 30, 1999, teaches a  
18 wastewater treatment system including an ozone mixer, a magnetic force, a filter, a  
19 second ozone mixer, a second magnetic force, an activated carbon reaction vessel and a  
20 second filter.

21 U.S. Patent No. 6,027,653 issued to Holland on February 22, 2000 teaches the  
22 utilization of a solidifying organic polymer-based filtration media and activated carbon  
23 placed in separate containers and arranged in an in-line, two phase process to extract

1 organic compounds and metals from feed streams containing emulsified or suspended  
2 concentrations of organic contaminants by absorbing and solidifying the organics into an  
3 easily retrievable, disposable mass.

4 Prior art methods have met with some success, however, they do not achieve the  
5 level of success of the system of current invention, which includes, among other things,  
6 injection of ozone prior to an electrocoagulation processing and re-circulation of the  
7 treated wastewater to re-charge an activated hydrocarbon filter.

#### 8 BRIEF SUMMARY OF THE INVENTION

9 Wastewater, such as bilge water, ballast water, and production pit waters with  
10 organic contaminants, is discharged to a sump located within a bermed area. By  
11 receiving the wastewater into a sump area, the bilge water input flow rate is independent  
12 of the treatment rate. The sump also allows for isolation of the wastewater from the  
13 environment by having the hydraulic column below the input point and berm wall. The  
14 wastewater is then pumped to a holding tank, typically capable of handling a day's  
15 operational volume. The wastewater is then pumped to an oil-water separator, where the  
16 oil is removed from the wastewater and decanted to a waste oil storage tank for pickup  
17 and recycling.

18 The remaining wastewater is pumped through an electrocoagulation process. The  
19 electrocoagulation process employs various sacrificial metals to coalesce the suspended  
20 and dissolved organics and inorganics. The electrocoagulation treated water is then  
21 transferred to a retention tank to give the contaminants time to coalesce and separate.  
22 The wastewater is decanted to a clean water holding tank through an activated carbon

1 filtration media. The activated carbon absorbs any remaining organics and acts as a filter  
2 for any solids present.

3 Ozone is injected at two points in the process. A small amount of ozone is  
4 injected prior to the electrocoagulation process. Some organics affect the  
5 electrocoagulation process. Injection of ozone reduces these contaminants and facilitates  
6 the electrocoagulation process. Ozone is also injected prior to the activated carbon. The  
7 ozone oxidizes the organics present in the wastewater. This reduces the load on the  
8 activated carbon. Water in the clean water-holding tank is circulated continuously  
9 through the activated carbon and the ozone injection zone. As the organics are reduced,  
10 the ozone will react with the organics captured by the activated carbon. This will purge  
11 the activated carbon extending the life of the activated carbon.

12 Sludge from the retention tank is periodically removed and treated for disposal.  
13 The sludge is pumped from the retention tank to a filter press, vacuum box or other  
14 methods to remove associated water. The sludge is optionally pumped to a mixer for  
15 further treatment, as required.

#### 16 BRIEF DESCRIPTION OF THE DRAWINGS

17 Figure 1 is a flow diagram of a waste water system of the invention.

#### 18 DESCRIPTION OF THE INVENTION

19 Fig. 1 depicts the inventive bilge water treatment system 10. The bilge water  
20 treatment system 10 comprises a sump 20, a holding tank 30, an oil/water separator 40, at  
21 least one electrocoagulation cell 50, a separation/retention tank 60, an ozone generator  
22 70, a carbon filter 80, and a discharge tank 90. The process for treating bilge water  
23 includes receiving wastewater influent, separating oil from the wastewater, injecting

1 ozone into the wastewater, using electrocoagulation to treat the wastewater, retaining the  
2 waste water to separate any flocculant and agglomeration, injecting more ozone into the  
3 waste water, filtering the waste water through activated carbon, treating sludge and  
4 discharging clean water.

5       Wastewater influent. A few of the most important factors to consider in receiving  
6 the wastewater such as bilge and ballast water is to reduce the time required to offload, to  
7 accept a variety of delivery methods, and to protect against spillage or environmental  
8 contamination. Several steps are required to achieve these goals. Multiple manifold  
9 ports 24 are set up to receive the incoming wastewater. This allows multiple offloading.  
10 A positive displacement pump 22 is located inside the berm (not shown) of the treatment  
11 plant. The manifold ports 24 have various adapters (not shown) allowing a variety of  
12 connections. The pump 22 produces a vacuum and lifts the wastewater from the vessel  
13 over the berm (not shown) to a sump 20, thus reducing the likelihood of a release to the  
14 environment. A sump tank 20 is used to isolate the wastewater in the bermed area from  
15 the environment. By utilizing a sump 20 below grade, hydraulic pressure cannot push the  
16 water up and out of the bermed area. The wastewater is pumped to a holding tank 30.  
17 This allows a larger volume of wastewater to be received during a treatment cycle.  
18 Should a pump or tank fail, the bermed area will contain the wastewater. There is no  
19 path outside of the containment area.

20       Treatment Phase I – Oil/Water Separation. A large component of bilge water and  
21 ballast water is free floating hydrocarbons. Removal of the free-floating hydrocarbons  
22 will allow the remainder of the process to operate more efficiently. This is accomplished  
23 by utilizing an oil/water separator 40. The wastewater is pumped into a location 42 near

1 the bottom of oil/water separator 40 through a diffuser 32 to slow the velocity. The  
2 volume of the separator 40 is sized to provide sufficient retention time for separation.  
3 Much of the suspended hydrocarbons will agglomerate and rise to the top of the tank 40  
4 if minimal energy, such as fluid velocity, is applied to the fluid column. In addition to  
5 the diffuser 32, baffles (not shown) are used to reduce the system energy. The  
6 hydrocarbons are allowed to rise and are decanted from the top of the separator tank 40 to  
7 a waste oil retention tank 44. Because the wastewater is pumped into the bottom 42 of  
8 oil/water separator 40, the rising hydrocarbons may be decanted from the top of oil/water  
9 separator 40. When wastewater is encountered during the decanting process, the  
10 decanting process is halted by stopping the pumping operation.

11 In order to decant as much oil as possible before wastewater is encountered, an  
12 insert 46 is placed in the top of the separator tank 40 to provide maximum differentiation  
13 of the oil/water column. Insert 46 is shaped such that the space 48 between insert 46 and  
14 the inside wall of oil/water separator 40 is reduced near the top of insert 46. By reducing  
15 the volume in the top portion of the oil/water separator 40, the surface area of the  
16 hydrocarbons floating on the top of the wastewater is reduced while the depth of the  
17 hydrocarbons is increased. This results in a greater vertical separation of the  
18 hydrocarbon/water interface. After being decanted from the wastewater, the  
19 hydrocarbons are stored until they can be processed for recycling.

20 Treatment Phase II – Ozone. An electrocoagulation process will be utilized in  
21 phase III. Electrocoagulation, however, has little effect on light-end hydrocarbons,  
22 alcohols and other aromatics. One of the limitations of the electrocoagulation process is  
23 the inability to place metal ions into the wastewater. Current flow between electrodes of

1 the electrocoagulation process is composed of electrons flowing to the positive electrode  
2 and metal ions flowing to the negative electrode. When contaminants act as a conduit for  
3 electron flow, the current flow is composed of mostly electrons. This reduces the metal  
4 ions available to affect treatment of the wastewater. To enhance phase III treatment of  
5 the decanted wastewater, a small amount of the ozone from the ozone generator 70 is  
6 diverted and injected through a venturi (not shown) into the wastewater prior to the  
7 electrocoagulation process. Ozone reacts slowly with complex aromatics and saturated  
8 aliphatics but will degrade many organic compounds, such as phenols and alcohols.  
9 Ozonation also results in polar and charged molecules that can react with polyvalent  
10 aluminum, created by the electrocoagulation process, to form precipitates. The end result  
11 is a decrease in turbidity, improved settlability and a reduction in the number of particles.  
12 Pre-ozonation destabilizes the colloids thus requiring less metal ion input from the  
13 electrocoagulation process 50. This also facilitates oxidation and removal of the  
14 inhibiting contaminants allowing the phase III process to operate more efficiently.

15 Treatment Phase III – Electrocoagulation. Some dissolved and suspended  
16 organics and inorganics remain in the wastewater. Additional steps are required to  
17 remove these contaminants prior to discharge.

18 Organic compounds remain in solution through several mechanisms. Mechanical  
19 agitation will shear the oil-water interface, creating small oil droplets, which become  
20 dispersed in the wastewater. Since systems drift towards a lower energy state, these  
21 droplets moving around as a result of convection, will normally coalesce, forming  
22 successively larger droplets, and eventually settle (or float) out of suspension.



1           Surfactants, present in the wastewater, gravitate toward the oil-water interface. A  
2 thin molecular coating of surfactants is adsorbed onto the surface of the oil droplet,  
3 resulting in such a polarization, that the droplets will repel each other and remain in a  
4 dispersed state. Smaller oil droplet size results in greater surface area and thus, a greater  
5 tendency to form a stable dispersion or emulsion, which can be difficult to remove from  
6 the wastewater.

7           The mechanism by which an electromotive force reduces the main stabilizing  
8 force of an emulsion is known as electrostriction. Under the influence of the  
9 electromagnetic field and electron flow created by the electrocoagulation process 50, the  
10 adsorbed ions, supplied by the surfactant and giving the oil droplet its surface charge, are  
11 less tightly held, and respond by moving over the droplet surface. This surface ion  
12 migration results in the formation of a dipolar charge on the oil droplets, which now can  
13 agglomerate under the force of mutual electrostatic attraction. Additionally, the dipolar  
14 droplets moving toward oppositely charged electrodes and in opposite directions can now  
15 collide and agglomerate until reaching a point where buoyancy overcomes their repulsive  
16 forces.

17           The electrocoagulation process 50 also generates small amounts of oxygen,  
18 hydrogen, and hydroxide radicals. This will further oxidize remaining hydrocarbons.

19           Colloids that remain in the wastewater are solid particles that remain suspended in  
20 water due to their small size and the forces acting upon them. In most cases, their size is  
21 100 nanometers or less. The particles tend to carry a surface electrical charge. These  
22 repulsive forces (Stem Forces) along with other forces such as Browning motion act to  
23 prevent the colloids from approaching close enough to interact with other particles (Van

1 der Waal forces) to form floc of sufficient size allowing gravitational forces to settle the  
2 floc. Thus, the particles will remain in suspension. The electrocoagulation process that  
3 results in removal of the remaining colloids consists of neutralizing the repulsive charges  
4 by placing ions or free radicals into the liquid. The result is a reduction of the repulsive  
5 forces allowing the colloids to coalesce and form a floc.

6 Flocculation incorporates coagulation of colloids along with other chemical  
7 processes such as metal oxide and hydroxide formation. These reactions form a stable  
8 floc that will settle out. Flocculation and separation by electrocoagulation is  
9 accomplished by three processes:

10 1. Double Layer Compression - the layers of ions of opposing charges  
11 surrounding the colloid particle are compressed by addition of large amounts of an  
12 electrolyte, reducing the sphere of influence of these charges and allowing them to  
13 approach close to the other colloids. This is achieved electrically by production of ions at  
14 the anode during oxidation.

15 2. Charge Neutralization - Inorganic coagulants (usually Al and  $Fe^{++}$ ) are  
16 applied to reduce surface charges on the colloid, which allows particle agglomeration.  
17 This involves absorption of a charged coagulant on the surface of the colloid, neutralizing  
18 the charge of the colloid's surface layer. The reduction of the surface charges allows  
19 particle agglomeration.

20 3. Bridging - In conventional applications, polymers or polyelectrolytes cause the  
21 formation of threads or fiber, which capture or bind colloids together in a bridging action  
22 to sweep the contaminants from the liquid. This occurs as a result of the large floc  
23 formation generated by the electrocoagulation process. The electrocoagulation process

1 also applies chemical precipitation. As atoms are released from a material, they form  
2 individual particles of dissociated ions in a solution. During electrocoagulation the  
3 process of dissolution is a result of the electrical forces applied to the solution. These  
4 ions can have a positive or negative charge. The positive charges are usually dissolved  
5 metals (cations) and are classified as inorganics. The negative charges are classified as  
6 organics or non-metals (anions). Once in solution the cations and anions are attracted to  
7 opposite charged ions in solution or to a source of charges such as the electrocoagulation  
8 plates.

9         This bridging process is described in the field as three separate reactions,  
10 cumulatively called migration. The first reaction includes the removal of positive ions,  
11 typically metal, from the electrocoagulation plates. As the positive ions, typically iron,  
12 aluminum or other metals, are released into the wastewater, the inorganic cations actively  
13 react with the contaminants in solution to form floc. Floc may be removed from the  
14 wastewater either by settling or by decanting.

15         The second reaction is electron interchange. During this reaction, electrons flow  
16 through the wastewater between the electrocoagulation plates, destabilizing some  
17 contaminants. It is this energy transfer that is required to initiate chemical reactions.  
18 This energy weakens the bond energy that holds molecules together. This weakened state  
19 allows other reactions to occur in the solution, which may cause the formation of a mass  
20 that may be removed from the wastewater

21         The third reaction is electrolysis. In the electrocoagulation process, most of the  
22 chemical reactions occur at the charge plates. The principal reaction is a reduction zone  
23 at the cathode, where hydrogen is formed, and an oxidation zone at the anode, where

1 oxygen and hydroxide are formed. These reactions facilitate a phase change for the  
2 dissolved contaminants. Contaminants that react with the oxygen, hydrogen or hydroxide  
3 flocculate at the electrocoagulation plates and may settle out or be decanted. Metals will  
4 form metal oxides or hydroxides and in some instances nitrates will form ammonia. The  
5 created floc and separated hydrocarbons are processed in the phase IV  
6 separation/retention tank 60.

7 Treatment Phase IV - Retention/Separation. The flocculation and agglomeration  
8 of contaminants requires a minimum of thirty minutes to form and begin the separation  
9 process. To accomplish this, the decanted and electrocoagulation treated wastewater is  
10 pumped into a retention/separation tank 60. The retention/separation tank 60 is sized to  
11 allow sufficient retention time for floc formation and separation. There are three zones  
12 within the retention/separation tank 60. Solid contaminants and the floc will fall to the  
13 bottom 62 of the retention/separation and accumulate as sludge to be processed in phase  
14 VII of the treatment process. The rag layer or floating contaminants will be removed  
15 periodically and treated with the sludge in phase VII. The remaining water has most of  
16 the contaminants removed. The treated water is then pumped to the discharge tank 90  
17 through the ozone 70 and activated carbon 80 process.

18 Treatment Phase V – Ozone. As discussed earlier, the oil/water separator 40 and  
19 the electrocoagulation process 50 will remove a majority of the contaminants from the  
20 wastewater. A small percentage of the organic and inorganic contaminants will not be  
21 removed and must be further processed to meet final discharge standards. Ozone ( $O_3$ ) is  
22 an allotrope of oxygen ( $O_2$ ). It is 1.5 times as dense as oxygen and 12.5 times more  
23 soluble in water. Ozone is injected into the wastewater prior to the activated carbon

1 process 80. Ozone injection provides numerous benefits. Oxidation of residual  
2 hydrocarbons is the primary function of ozone in this process 70. Other characteristics of  
3 ozone are desirable. Disinfection by ozone takes place by rupture of the cell wall. Ozone  
4 levels of 0.4 ppm in wastewater for 4 minutes have been shown to kill any bacteria, virus,  
5 mold and fungus in the wastewater. To insure that no biological processes begin in the  
6 discharge tank 90 or on the activated carbon matrix 80, the water is recirculated through  
7 the ozone injection system 70, the activated carbon system 80 and the discharge tank 90.  
8 Any microorganism that passes through the system or enters from the outside is  
9 eradicated. The ozone is injected into the bottom of the clean water tank. This facilitates  
10 the efficiency of the transfer of  $O_3$  into the water column. The ozone process 70 will  
11 react with contaminants that may remain in the wastewater creating less offensive  
12 compounds such as oxidizing sulfides to sulfates. Ozone will oxidize transition metals to  
13 higher oxidation states in which they usually form less soluble oxides, which are easier to  
14 filter. Finally, the ozone is used to regenerate the activated carbon 80. Any  
15 hydrocarbons not destroyed by the system will be adsorbed by the activated carbon 80.  
16 During periods when no hydrocarbons are present in the treated water, the recirculation  
17 process will carry ozonated water through the activated carbon 80. Hydrocarbons  
18 adsorbed by the activated carbon will be oxidized, thus regenerating the activated carbon  
19 80.

20 Treatment Phase VI - Activated Carbon. Where ozone reacts rapidly with most  
21 simple aromatic compounds and unsaturated aliphatics, activated carbon will adsorb the  
22 larger organic chains and, depending upon the granular structure, will act as a filter.  
23 Activated carbon works by attracting and holding certain chemicals as water passes

1 through it. Activated carbon is a highly porous material; therefore, it has an extremely  
2 high surface area for contaminant adsorption. Adsorption is caused by London  
3 Dispersion Forces, a type of Van der Waals force, which exists between molecules. The  
4 force acts in a similar way to gravitational forces between planets. Much like the  
5 electrocoagulation process 50, London Dispersion Forces are extremely short ranged and  
6 therefore sensitive to the distance between the carbon surface and the adsorbate molecule.  
7 They are also additive; meaning the adsorption force is the sum of all interactions  
8 between all the atoms. The adsorption process depends on the following factors:

9       1. Physical properties of the activated carbon, such as pore size distribution and  
10 surface area;

11       2. The chemical nature of the carbon source, or the amount of oxygen and  
12 hydrogen with which it is associated;

13       3. Chemical composition and concentration of the contaminant such as its  
14 molecular weight;

15       4. A higher number of functional groups such as double bonds or halogen  
16 compounds;

17       5. Increasing polarisability of the molecule, which is related to the electron  
18 clouds of the molecule;

19       6. The temperature and pH of the water; and

20       7. The flow rate or time exposure of water to the activated carbon.

21 Forces of physical attraction or adsorption of contaminants to the pore walls is the  
22 most important activated carbon filtration process 80. The amount and distribution of  
23 pores play key roles in determining how well contaminants are filtered. The best

1 filtration occurs when pores are barely large enough to admit the contaminant molecule.  
2 Because contaminants exist in the wastewater in a range of sizes, they are attracted  
3 differently depending on pore size of the filter. In general, activated carbon filters are  
4 most effective in removing contaminants that have relatively large molecules. Water  
5 temperature, pH and exposure times are also considered in this process. The  
6 electrocoagulation process in phase III tends to lower the pH of the wastewater.  
7 Recirculation produces sufficient exposure to increase adsorption. Processes other than  
8 physical attraction also affect activated carbon filtration. The filter surface may actually  
9 interact chemically with organic molecules.

10 Also, electrical forces between the activated carbon surface and some  
11 contaminants may result in adsorption or ion exchange. The type of activated carbon to  
12 achieve maximum adsorption of the contaminants present is considered in this process.

13 Treatment Phase VII - Sludge Treatment. The residue from the treatment process  
14 in separator tank 40 and retention/separation tank 60 are removed and passed through a  
15 drying chamber (not shown). This portion of the process can be any process that will  
16 allow any residual water to pass while retaining solid particles, removed contaminants or  
17 floc formed by the various process such as a filter press, a vacuum box, centrifuge, drying  
18 bed or drying box. The solid material is treated to pass the paint filter test for disposal.  
19 Should contaminants removed from the wastewater result in a characteristic solid waste;  
20 the material is chemically treated to render it non-hazardous.

21 Treatment Phase VIII - Clean Water Discharge. The treated wastewater is held in  
22 a retention tank 90 for testing, then discharged. This tank 90 is sized to provide sufficient  
23 depth for the ozone contact time.

1           The foregoing disclosure and description of the invention is illustrative and  
2   explanatory thereof. Various changes in the details of the illustrated construction may be  
3   made within the scope of the appended claims without departing from the spirit of the  
4   invention. The present invention should only be limited by the following claims and their  
5   legal equivalents.